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(54) Title: COMPOSITIONS AND METHODS FOR POLISHING SEMICONDUCTOR WAFERS

(57) Abstract

Stable dispersions of submicron abrasive particles are provided by using an amino alcohol as a stabilizing component. A composition is provided, suitable for polishing an insulating or barrier layer, comprising: water, an aqueous dispersion of submicron abrasive particles for which an amino alcohol is used as a stabilizing component, and a chemically interactive component which interacts with the surface being polished. Also provided is an additive for CMP polishing slurries which is an organic polymer having a degree of polymerization of at least five, the polymer having a plurality of moieties with affinity to surface groups on the surface being polished.

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COMPOSITIONS AND METHODS FOR POLISHING SEMICONDUCTOR WAFERS

This application claims the benefit of copending provisional application 60/112,601 filed December 17, 1998.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to compositions which are useful as slurries used during the chemical mechanical polishing of substrates, especially those comprised of silica, silicates or silicon nitride.

Description of Related Art

During the chemical-mechanical polishing (CMP) of interlayer dielectrics used in the manufacture of integrated circuits a slurry is used in conjunction with a polishing pad to facilitate the removal of an insulator or dielectric material. In most CMP applications this insulating or dielectric material is SiO_2. In an aqueous environment the surface undergoes a hydration reaction with H_2O to produce a surface network of hydroxylated Si molecules. Dissolution of this network generally occurs above a pH of 9.0 because of the solubility of the reaction product at high pH. Also, a high pH is desirable to achieve a high removal rate. Silicon Nitride, while chemically dissimilar to SiO_2, has shown generally similar polishing behavior. Thus, formulations shown to be suitable for the polishing of SiO_2 are also effective for silicon nitride, albeit at lower rates. To achieve this high pH, bases such as KOH and NH_4OH are used to yield a pH of 10-11 in commercial production of polishing slurries useful for CMP of insulating layers.

For example, Yu et al. in USP 5,244,534 describe a CMP step for removing insulation material from around a metal plug. To remove an oxide insulation material, such as SiO_2, they describe the use of a colloidal silica slurry containing etchants selective to the oxide, such as a basic mixture of H_2O and KOH. (col.4, lines 59-64).

It is imperative in the slurries useful for CMP removal of insulating materials that the dispersions of silicon dioxide particles upon which these slurries are based be stable. It is an object of this invention to provide dispersions of silicon dioxide which do not gel or settle out and, if there is sedimentation, that the sediment be easily redispersed. A further object of this invention is to provide slurries useful for the chemical-mechanical polishing of insulation layers on semiconductor wafers which are stable and provide a high quality surface for the semiconductor wafers upon polishing.

SUMMARY OF THE INVENTION

Stable dispersions of submicron abrasive particles are provided by using an amino alcohol as a stabilizing component.

A composition is provided, suitable for polishing an insulating or barrier layer, comprising: water, an aqueous dispersion of submicron abrasive particles for which an amino alcohol is used as a stabilizing component, and a chemically interactive component which interacts with the surface being polished, such as potassium hydroxide or ammonium hydroxide. The composition provided is most useful when the pH of the composition is adjusted to between 9 and 12.

A polymer additive for a CMP slurry which provides a polished surface with less surface roughness and fewer scratches than when the slurry is used without such an additive is another aspect of this invention. The additive is defined as an organic polymer having a degree of polymerization of at least five comprising a plurality of moieties having affinity to surface groups contained on insulating layer surfaces. These groups are commonly polar moieties, such as, but not limited to, hydroxy, carboxy, carbonyl, alkoxy, sulphonyl, and phosphonyl. Examples of this type of molecule include poly-vinyl alcohol, poly-vinylpyrrolidone, poly-methyl methacrylate, poly-formaldehyde, poly-ethylene oxide, poly-ethylene glycol, and poly-methacrylic acid. This additive is disclosed in Patent Application Serial Number 09/329,225 which is made a part of this specification by reference. In the previous application, the additive was made a part of the CMP slurry to provide silica rate suppression. The polymer

additive in the present invention provides a polished surface with less surface roughness and fewer scratches.

A further aspect of the present invention is a process for polishing insulating layers in which the slurry, used in combination with a standard polishing machine and a polishing pad, is comprised of water, an aqueous dispersion of submicron abrasive particles for which an amino alcohol is used as a stabilizing component, and a chemically interactive component that interacts with the surface being polished. The composition provided is most useful when the pH of the composition is adjusted to between 9 and 12.

A further aspect of the present invention is a process for CMP of a semiconductor wafer in which the slurry, used in combination with a standard polishing machine and a polishing pad, comprises an organic polymer having a degree of polymerization of at least five with a plurality of moieties having affinity to surface groups contained on insulating layer surfaces.

DETAILED DESCRIPTION OF THE INVENTION

Commonly hydroxides, such as potassium hydroxide, ammonium hydroxide, and sodium hydroxide, and amines have been used as dispersing agents for CMP slurry abrasives. It has been found that a class of compounds known as amino alcohols provide excellent dispersion results both in the predispersed abrasive concentrates and in the CMP slurry compositions which are made from the predispersed abrasive concentrates.

EXAMPLE 1

Four abrasive concentrates each containing 25% by weight of silica particles were made from NAC A-70 milled silica (fumed silica powder available from Nippon Areosol Corp., surface area 70 - 100 m^2/g).

Table 1

Sample	Dispersing Agent	Weight %	pH	5 week Sediment Height, mm	5 week Redispersability
A	AMP-95	3.4	11.2	2.3	total
B	DMAMP-80	2.5	11.2	5	total
C	TRIS AMINO®	5.0	10.1	thin film	total
D	45% KOH	1.15	11.1	5	partial

The above amino alcohols may be obtained from ANGUS Chemical Company, Buffalo Grove, IL. The above compounds are: AMP, 2-amino-2-methyl-1-propanol; DMAMP, 2-dimethylamino-2-methyl-1-propanol; and TRIS AMINO®, tris(hydroxymethyl)aminomethane.

Amino alcohols are defined as organic compounds which contain at least one amino group and one hydroxyl group.

To provide stability amino alcohols may be used at 0.01% to 10% by weight in the aqueous dispersions of submicron abrasive particles according to this invention.

Submicron abrasive particles which might be stabilized with the amino alcohols include, but are not limited to, silica, ceria, alumina, titania, and silica gel. The submicron abrasive particles should have a primary particle size in the range of 5 nanometers to 100 nanometers. Primary particle size can be determined by TEM imaging where the smallest particles are measured even if shown as part of an agglomeration.

Slurries A and B above when used for CMP of a silicon dioxide surface show no removal of the silicon dioxide surface. These tests were carried out on a Strasbaugh 6DS-SP polishing machine under the following conditions: Time, 120 sec; Down force, 7 psi; Back pressure, 0.5 psi; Platen speed, 20 rpm; Carrier speed, 15 rpm; Temperature, 21°C; Slurry flow, 125 ml/min; Slurry dilution ratio, 1:1 with DI water; Pad type, conventional urethane pad.

Commonly used insulating layers found on semiconductor wafers are silicon dioxide, silicates, TEOS, and BPSG. These insulating materials as well as some barrier layers, such as silicon nitride, can be effectively polished with CMP slurries of this invention.

EXAMPLE 2

In order to be an effective slurry for use in the polishing of an insulating or barrier layer surface, the stabilized abrasive particles of this invention must have along with them a chemically interactive component that interacts with the surface being polished, such as potassium hydroxide or ammonium hydroxide. The following Table 2 illustrates this fact, plus the fact that the addition of a small amount of a compound may provide a polished surface with less surface roughness and fewer scratches than when the slurry is used without such a compound. This compound is defined as an organic polymer having a degree of polymerization of at least five with a plurality of moieties having affinity to surface groups contained on insulating layer surfaces. These groups are commonly polar moieties, such as, but not limited to, hydroxy, carboxy, carbonyl, alkoxy, sulphonyl, and phosphonyl. Examples of this type of molecule include poly-vinyl alcohol, poly-vinylpyrrolidone, poly-methyl methacrylate, poly-formaldehyde, poly-ethylene oxide, poly-ethylene glycol, and poly-methacrylic acid. In the slurries of Table 2 PVP (poly-vinylpyrrolidone) is used for this purpose.

As in Example 1, the polishing tests on TEOS wafers shown in Table 2 were carried out on a Strasbaugh 6DS-SP polisher under the following conditions: Time, 120 sec; Down force, 7 psi; Back pressure, 0.5 psi; Platen speed, 51 rpm; Carrier speed, 41 rpm; Temperature, ambient; Slurry flow, 125 ml/min; Slurry dilution ratio, 1:1 with DI water; Pad type, conventional urethane pad.

Table 2

Slurry	Composition Weight %	SiO_2 RR Å/min	Roughness RMS nm	P-V nm
E	25% A-70, 1.7% TA	0		
F	E + 2.35% NH_4OH(30%)	1600	.40	5.1
G	E + 0.38% KOH	1800	.30	3.9
H	G + 0.2% PVP	1800	.26	3.9
J	20% A-130, 1% TA	0		
K	J + 1.08% NH_4OH (30%)	1500	.40	5.5
L	J + 0.36% KOH	1600	.42	5.2
M	L + 0.2% PVP	1900	.28	5.0

A-70 = fumed silica powder with a surface area of 70 - 100 m^2/g

TA = Tris(hydroxymethyl)aminomethane

PVP = poly-vinylpyrrolidone

A-130 = fumed silica powder with a surface area of 120 - 140 m^2/g

It is obvious from the above table that a compound which interacts with the surface being polished must be added to an abrasive particle slurry in order to get removal of an insulating layer.

The table also shows the improvement in surface roughness which occurs upon addition of an organic polymer (PVP) to a CMP slurry. The surface measurements were obtained using an Atomic Force Microscope (AFM) available from Digital Instruments, Inc. Using the tapping mode, a silicon tip, and a measurement area of 10 microns by 10 microns, the root mean square (RMS) roughness and the peak to valley (P-V) roughness were determined. Surface condition can be observed from the images

provided by the AFM. Figures 1 to 4 show AFM images of the wafer surfaces after polishing with slurries G, H, L, and M. These images dramatically show the improvement in surface condition when using an organic polymer in the slurries. Such a polymer would typically be used in concentrations of 0.01% to 5% in the slurries of this invention.

The present invention may be embodied in forms other than those shown above so that one should look to the claims below rather than the foregoing specification as indicating the scope of the invention.

CLAIMS

1. A stable dispersion of submicron abrasive particles in which an amino alcohol is a stabilizing component.

2. A stable dispersion according to claim 1 wherein said submicron abrasive particles are silica.

3. A stable dispersion according to claim 1 wherein said amino alcohol is from the group consisting of 2-amino-2methyl-1-propanol, 2-dimethylamino-2-methyl-1-propanol, and tris(hydroxymethyl)aminomethane.

4. A stable dispersion according to claim 3 wherein said amino alcohol is tris(hydroxymethyl)aminomethane.

5. A composition suitable for polishing an insulating or barrier layer comprising: water, an aqueous dispersion of submicron abrasive particles for which an amino alcohol is used as a stabilizing component, and a chemically interactive component which interacts with the surface being polished.

6. A composition according to claim 5 wherein said chemically interactive component is from the group consisting of potassium hydroxide and ammonium hydroxide.

7. A composition according to claim 5 also comprising an organic polymer having a degree of polymerization of at least five, said polymer having a plurality of moieties with affinity to surface groups on said semiconductor wafer surface.

8. A composition according to claim 5 wherein said submicron abrasive particles are silica.

9. A composition according to claim 5 wherein said amino alcohol is from the group consisting of 2-amino-2methyl-1-propanol, 2-dimethylamino-2-methyl-1-propanol, and tris(hydroxymethyl)aminomethane.

10. A composition according to claim 9 wherein said amino alcohol is tris(hydroxymethyl)aminomethane.

11. A composition according to claim 5 wherein the pH is adjusted to within 9 to 12.

12. A method for polishing a semiconductor wafer having an insulating layer or barrier layer wherein the surface of said workpiece is exposed to a polishing composition comprising: water, an aqueous dispersion of submicron abrasive particles for which an amino alcohol is used as a stabilizing component, and a chemically interactive component which interacts with the surface being polished.

13. A method according to claim 11 wherein said chemically interactive component is from the group consisting of potassium hydroxide and ammonium hydroxide.

14. A method according to claim 11 also comprising an organic polymer having a degree of polymerization of at least five, said polymer having a plurality of moieties with affinity to surface groups on said semiconductor wafer surface.

15. A method according to claim 11 wherein said submicron abrasive particles are silica.

16. A method according to claim 11 wherein said amino alcohol is from the group consisting of 2-amino-2methyl-1-propanol, 2-dimethylamino-2-methyl-1-propanol, and tris(hydroxymethyl)aminomethane.

17. A method according to claim 15 wherein said amino alcohol is tris(hydroxymethyl)aminomethane.

18. A method according to claim 11 wherein the pH of said composition is adjusted to within 9 to 12.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/30154

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C09G 1/02; CO9K 3/14
US CL :51/307, 308, 308; 106/3; 438/692, 693; 510/175, 395, 396, 397
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 51/307, 308, 308; 106/3; 438/692, 693; 510/175, 395, 396, 397

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

none

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,867,757 A (PAYNE) 19 September 1989 (19/09/89), see entire document.	1-18
Y	US 4,462,188 A (PAYNE) 31 July 1984 (31/07/84), see entire document.	1-18
Y	US 4,169,337 A (PAYNE) 02 October 1979 (02/10/79), see entire document.	1-18
Y	US 4,752,628 A (PAYNE) 21 June 1988 (21/06/88), see entire document.	1-18
Y	US 4,892,612 A (HUFF) 09 January 1990 (09/01/90), see entire document.	1-4
Y	US 4,284,533 A (IMAMURA et al.) 18 August 1981 (18/08/81), see the claims.	1-11

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,284,533 A (IMAMURA et al.) 18 August 1981 (18/08/81), see the claims.	1-11
Y	Derwent Acc-No: 1978-24860A, based on SU 516728A abstract, 23 June 1977, ANRYUSHCH et al., "Metal polishing paste-comprises an amino alcohol, soap, glycol and abrasive".	1-5,7-11
Y	Derwent Acc-No: 1979-29172B, based on SU 608823A abstract, 16 May 1978, BAGDASAROV et al., "Aqueous polishing composition for metallic, e.g. copper, mirrors-contains diamond powder and also ammonia and hydroxyalkylated aminoalcohol, used for optical mirrors".	1-5,9-11